Tetrahedron Vol. 41, No. 11, pp. 2207 to 2214, 1985
Printed in Great Britain.

0040–4020/85 $3.00 + .00

PHOTO-OXYGENATION OF 1,2-DIARYLCYCLOPROPANES VIA ELECTRON TRANSFER

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(*Received in Japan* 7 *May* 1984)

Abstract—The photo-oxygenation of 1,2-diarylcyclopropanes bearing electron-donating substituents in the presence of 9,10-dicyanoanthracene (DCA) in acetonitrile affords *trans*- and *cis*-3,5-diaryl-1,2-dioxolanes in excellent yields. The DCA-sensitized photo-oxygenation of less electron-rich 1,2-diarylcyclopropanes gives various oxidation products in low yields. These photoreactions are greatly accelerated by the addition of certain aromatic hydrocarbons and metal salts, and are completely quenched by the addition of triethylamine and 1,4-diazabicyclo[2.2.2]octane. No photo-oxygenation takes place in non-polar solvents. The electron transfer mechanism is proposed for the photo-oxygenations, in which the cation radicals of 1,2-diarylcyclopropanes are involved as chain carriers.

Electron transfer photo-oxygenation of electron-rich organic substrates has drawn considerable attention from synthetic and mechanistic viewpoints in recent years.[1–13] For this reaction, three mechanisms (Eqs 1–7) have been proposed. The first involves the reaction between the substrate cation radical ($D^{+\cdot}$) and the superoxide ion ($O_2^{-\cdot}$) which is generated via electron-transfer from an electron acceptor anion radical ($A^{-\cdot}$) to a ground state molecular dioxygen ($^3O_2$) (Eqs 1–3).[1] The second mechanism involves the reaction between $D^{+\cdot}$ and $^3O_2$ (Eqs 4 and 5)[2] and the third mechanism involves electron transfer from substrate (D) to singlet oxygen ($^1O_2$) which is generated by a dye-sensitized photoreaction of $^3O_2$ or by decomposition of endoperoxide (Eqs 6 and 7).[3] The substrates so far examined include alkenes,[1,4] alkadienes,[2] alkynes,[5] sulphides[6] and some aromatic compounds,[7,8] but little is known about the photo-oxygenation of a carbon–carbon single bond. Such a photoreaction is expected to occur with small ring compounds because of their ring strain and electron-donating ability.[9,14] We now report that electron-donor 1,2-diarylcyclopropanes efficiently undergo photo-oxygenation to give 3,5-diaryl-1,2-dioxolanes when the reaction is carried out in a polar solvent in the presence of 9,10-dicyanoanthracene (DCA) as electron acceptor.[15] We also demonstrate that certain aromatic hydrocarbons and metal salts serve as a cosensitizer for this photo-oxygenation and discuss the mechanism of the photoreaction and the cosensitization.

$$A + D \xrightarrow{h\nu} A^{-\cdot} + D^{+\cdot} \tag{1}$$

$$A^{-\cdot} + {}^3O_2 \rightarrow A + O_2^{-\cdot} \tag{2}$$

$$D^{+\cdot} + O_2^{-\cdot} \rightarrow DO_2 \tag{3}$$

$$D^{+\cdot} + {}^3O_2 \rightarrow DO_2^{+\cdot} \tag{4}$$

$$DO_2^{+\cdot} + D \rightarrow DO_2 + D^{+\cdot} \tag{5}$$

$$D + {}^1O_2 \rightarrow D^{+\cdot} + O_2^{-\cdot} \tag{6}$$

$$D^{+\cdot} + O_2^{-\cdot} \rightarrow DO_2 \tag{7}$$

RESULTS

DCA-sensitized photo-oxygenation of 1,2-*diarylcyclopropanes in the absence of additive*

Irradiation of an oxygen saturated acetonitrile solution of *trans*-1,2-bis(4-methoxyphenyl)cyclopropane (**1c**) in the presence of a catalytic amount (1/200 equivalent) of DCA with a high-pressure mercury arc through an aqueous NH_3–$CuSO_4$ filter solution (405 nm light) gave *trans*- and *cis*-3,5-bis(4-

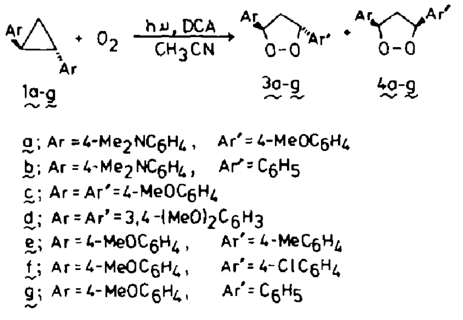
Table 1. DCA-sensitized photo-oxygenation of 1,2-diarylcyclopropanes (**1a**–**1j**)

Cyclopropane	Irradiation time (h)	Total yield[a] (%)	Product ratio (%) 3	4	5	6	7
1a	4.5	90[b]	30	70	0	0	0
1b	4.5	95[b]	30	70	0	0	0
1c	4.5	95	23	77	0	0	0
1d	4.5	80[b]	24	76	0	0	0
1e	4.5	95	25	75	0	0	0
1f	4.5	95	25	75	0	0	0
1g	4.5	95	22	78	0	0	0
1h	32	21	0	0	44	40	16
1i	32	17	0	0	52	29	19
1j	32	19	0	0	48	35	17

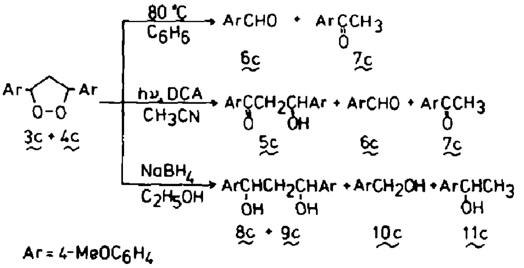
[a] Total yields based on the cyclopropanes used.
[b] A mixture of *trans*- and *cis*-1,2-dioxolanes was obtained.

methoxyphenyl)-1,2-dioxolanes (**3c** and **4c**) in 95% yield (Table 1). Under continuous oxygen bubbling, **1c** was oxidized in a much shorter time, giving **3c** and **4c** in >90% yield. The product ratio of **3c**–**4c** remained constant (**3c**–**4c** = 0.3) up to 98% conversion under both conditions. These products were isolated by repeated recrystallizations of the reaction mixture from hexane. Their structures were assigned from elemental analyses and spectral properties and also by chemical transformations. The ^{1}H-NMR spectrum of **3c** showed a sharp triplet signal at δ 2.92 which is assignable to the methylene group placed at a magnetically symmetrical environment. On the other hand, the ^{1}H-NMR spectrum of **4c** showed two double triplet signals centred at δ 2.65 and 3.34, indicating that this compound has a magnetically unequivalent methylene group.

Photolysis of a mixture of **3c** and **4c** in acetonitrile using DCA as sensitizer gave 1,3-bis(4-methoxyphenyl)-1-hydroxypropan-3-one (**5c**), 4-methoxybenzaldehyde (**6c**) and 4-methoxyacetophenone (**7c**) in a ratio of 4 : 2 : 1. Thermolysis of **3c** and **4c** in refluxing benzene under a nitrogen atmosphere gave, quantitatively, **6c** and **7c** in a ratio of 1 : 1. Chromatography on silica gel gave the decomposed products, **5c**, **6c** and **7c**. Treatment of a mixture of **3c** and **4c** with NaBH$_4$ gave 1,3-bis(4-methoxyphenyl)propane-1,3-diol as a mixture of the *meso* and *dl* isomers (**8c** and **9c**), 4-methoxyphenylmethanol (**10c**) and 1-(4-methoxyphenyl)ethanol (**11c**) in a ratio of 1 : 1 : 1. All these results are consistent with the assigned structures for **3c** and **4c**.



Scheme 1.



Scheme 2.

When *cis*-1,2-bis(4-methoxyphenyl)cyclopropane (**2c**) was irradiated under similar conditions, the rapid isomerization of **2c** to **1c** was observed at the initial stage.[16,17] Further irradiation of the reaction mixture yielded **3c** and **4c** in the ratio identical with that in the photoreaction of **1c**.

The photoreaction of other 1,2-diarylcyclopropanes, **1a**, **1b** and **1d**–**1g**, which bear electron-donating substituents and, hence, have lower oxidation potentials (Table 2), gave the corresponding 1,2-

Table 2. Rate constants for the fluorescence quenching of DCA, oxidation potentials of cyclopropane derivatives and other compounds, and calculated ΔG values for the one-electron transfer process from the compounds to ^{1}DCA* in acetonitrile

Compound	$k_q\tau$ (mol^{-1} l s)	k_q^{a} (mol^{-1} l)	$E^{ox}_{p/2}$ (V) (Ag/Ag$^+$)	ΔG^{b} (kJ mol^{-1})
1a	442	3.45	—	—
1b	326	2.55	0.25	−132.2
1c	234 (148^c)	1.83	0.55	−103.2
1d	246	1.92	0.55	−103.2
1e	230	1.80	—	—
1f	218	1.70	—	—
1g	218	1.70	0.75	−83.9
1h	199	1.55	0.90	−69.5
1i	183	1.43	1.06	−54.0
1j	180 (78^c)	1.41	1.14	−46.3
2c	207	1.62	0.65	−93.6
Phen	219	1.71	1.17^d	−43.4
BP	45	0.35	—	—
TEA	293	2.29	0.48	−110.0
DABCO	358	2.80	0.31	−126.4
DMB	261	2.04	0.95	−64.6
DCA	—	—	(−1.33)^e	—

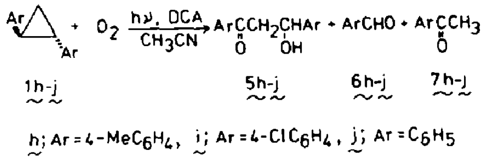
[a] Rate constant for fluorescence quenching calculated from Stern–Volmer plots in aerated acetonitrile solutions. τ(DCA, air) = τ(DCA, N$_2$) × I (DCA, air)/I (DCA, N$_2$) = 12.8 ns. [τ (DCA, N$_2$) = 15.3 ns].[2]

[b] The calculated values by application of Eq. (8): the excited singlet energy of DCA, 2.89 eV; the energy of Coulomb force, 0.06 V.[22,23]

[c] The values in aerated benzene solutions.

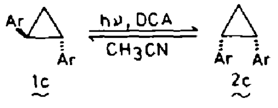
[d] The value from Ref. 19.

[e] Reduction potential.



Scheme 3.

dioxolanes **3a**, **3b** and **3d**–**3g** and **4a**, **4b** and **4d**–**4g** in excellent yields. On the other hand, the photoreaction of the cyclopropanes **1h**–**1j**, which have higher oxidation potentials than **1a**–**1g**, under similar conditions afforded a variety of oxidized products **5h**–**5j**, **6h**–**6j** and **7h**–**7j** in poor yields after prolonged irradiation. It is conceivable that, in these cases, the 1,2-dioxolanes are produced at slow rates, but they decompose rapidly to the corresponding ketoalcohols, aldehydes and ketones under irradiation conditions. The results are summarized in Table 1.



Scheme 4.

DCA-sensitized photo-oxygenation of 1,2-diarylcyclopropanes in the presence of aromatic hydrocarbons

The rates of formation of the 1,2-dioxolanes by the DCA-sensitized photoreaction of the cyclopropanes was remarkably accelerated by the addition of aromatic hydrocarbons, such as phenanthrene (Phen) and biphenyl (BP), to the reaction systems.[10]† For example, irradiation of an acetonitrile solution of **1c** containing 1/200 equivalent of DCA and a ½ equivalent of Phen under continuous oxygen bubbling rapidly gave **3c** and **4c** in quantitative yields. The rate of formation of **3c** and **4c** in the presence of Phen was 5–10 times faster than that in the absence of Phen, but the product ratio **3c**–**4c** was the same both in the presence and absence of Phen. The other aromatic hydrocarbons, such as naphthalene and pyrene, also accelerated the photoreaction of **1c**. However, when crystalline aromatic hydrocarbons were used as accelerating agents, it was found that separation of the dioxolanes from the reaction mixtures becomes difficult, whereas when liquid aromatic hydrocarbons, such as 1-methylnaphthalene (MeNaph) and *p*-xylene (*p*-Xy) were used, the dioxolanes could be easily isolated by recrystallization of the reaction mixture from hexane after filtration of sparingly soluble DCA, although side chain methyl groups of these aromatic hydrocarbons were partially oxidized.[7]

Similar DCA-sensitized photo-oxygenation of **1h**–**1j** did not give the corresponding 1,2-dioxolanes but efficiently produced the oxidized products **5h**–**5j** and **6h**–**6j** in the presence of aromatic hydrocarbons. Particularly, when MeNaph and *p*-Xy were used as accelerating agent, **1h**–**1j** and the aromatic hydrocarbons were oxidized at the same time, giving a complex mixture of oxidized products (Table 3).

Pyrene-sensitized photo-oxygenation of **1c** *in the presence of* 1,4-*dicyanobenzene*[19–21]

Irradiation of an acetonitrile solution of **1c** containing pyrene and 1,4-dicyanobenzene (DCB) as sensitizer in an oxygen atmosphere afforded **3c** and **4c** in the same ratio as for the DCA-sensitized photoreaction. Although this pyrene-sensitized photo-oxygenation occurred efficiently, giving the dioxolanes in high yields, it was also found that isolation of the dioxolanes from the reaction mixture in a pure state is difficult. This photo-oxygenation did not occur in benzene.

Solvent effects on the DCA-sensitized photo-oxygenation of **1c**

The reactivity of **1c** in the DCA-sensitized photo-oxygenation strongly depended on the solvent polarity. Indeed, the relative rates for the formation of **3c** and **4c** decreased with decreasing solvent polarity: $CH_3CN > C_2H_5CN > C_3H_7CN$ (Table 4). In the less polar solvents, most of the starting material was recovered even after prolonged irradiation.

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† Co-sensitization by aromatic compounds in photo-induced electron transfer-mediated reactions has been reported by several groups.[18] See also Ref. 19.

Table 3. DCA-sensitized photo-oxygenation of 1,2-diarylcyclopropanes (**1c** and **1j**) in the presence of additives[a]

Cyclopropane	Additive (mol/l)	Irradiation time (h)	Total[b] yield (%)	Product ratio (%)	
				3+**4**	**5**+**6**+**7**
1c	None	4.5	95	>99	<1
1c	Phen (0.0125)	1.0	>95	>97	<3
1c	BP (0.0125)	1.0	>95	>97	<3
1c	MeNaph (0.0125)	1.0	>95	>97	<3
1c	*p*-Xy (0.1)	2.0	85	>97	<3
1c	$LiBF_4$ (0.0125)	1.0	>95	>99	<1
1c	$Mg(ClO_4)_2$ (0.0125)	1.0	>95	>99	<1
1c	TEA (0.0125)	4.5	0	—	—
1c	DABCO (0.0125)	4.5	0	—	—
1j	None	32	19	<1	>99
1j	Phen (0.0125)	5.0	85	<1	>99

[a] [**1c**] = [**1j**] = 0.025 mol/l in acetonitrile under an O_2 atmosphere.
[b] Total yields based on the cyclopropanes used.

Table 4. Solvent effect on the DCA-sensitized photo-oxygenation of **1c**

Solvent	Dielectric constant (ε)	Irradiation time (h)	Yield of **3c** and **4c** (%)	Relative rate
CH_3CN	37.5	4.5	95	1
C_2H_5CN	27.2	4.5	58	0.6
C_3H_7CN	20.3	4.5	29	0.3
CH_2Cl_2	8.9	9.0	0	0
CH_3CO_2Et	6.0	9.0	0	0
C_6H_6	2.3	9.0	0	0

Effects of cation radical quenchers on the DCA-sensitized photo-oxygenation of **1c**

The formation of **3c** and **4c** in the DCA-sensitized photo-oxidation of **1c** in acetonitrile was efficiently quenched by the addition of triethylamine (TEA) and 1,4-diazabicyclo[2.2.2]octane (DABCO), whose oxidation potentials are lower than **1c** (Table 2). At high concentration of these amines, the formation of **3c** and **4c** was completely quenched with a quantitative recovery of **1c**. The fluorescence of DCA was also quenched by these amines at a diffusion controlled rate. However, the formation of **3c** and **4c** was only partially quenched by the addition of 1,4-dimethoxybenzene (DMB) which has higher oxidation potential than **1c**.

DCA-sensitized photo-oxygenation of 1,2-diarylcyclopropanes in the presence of metal salts

The DCA-sensitized photo-oxygenation of the cyclopropanes was also accelerated by the addition of metal salts, such as $LiBF_4$ and $Mg(ClO_4)_2$. For example, irradiation of acetonitrile solutions of **1c**–**1f**, containing a catalytic amount of DCA and $LiBF_4$ (1/2 equivalent) under an oxygen stream, afforded the corresponding 1,2-dioxolanes **3c**–**3f** and **4c**–**4f** in excellent yields ($>95\%$) along with a small amount of the corresponding benzaldehyde derivatives ($<3\%$) (Table 3). On the other hand, the addition of LiCl and LiBr into the reaction system partially quenched the formation of **3c** and **4c**.

Fluorescence quenching and redox properties

The rate constants, k_q, for the fluorescence quenching in benzene and acetonitrile under aerated conditions are shown in Table 2. The values of k_q were calculated from the slopes of the Stern–Volmer plots.[22] In acetonitrile, the fluorescence of DCA was quenched by all the cyclopropane derivatives examined at a nearly diffusion controlled rate. No exciplex emission was observed in either solvent.

Table 2 also shows the oxidation potentials of the representative cyclopropane derivatives and the reduction potentials of DCA in acetonitrile against an Ag/Ag^+ reference electrode. From these data, the free energy changes (ΔG) for the one-electron transfer process from the cyclopropane derivatives to the excited singlet DCA ($^1DCA^*$) were estimated by application of the Rehm–Weller equation, where $E(D/D^+)$ and $E(A^-/A)$ are the oxidation potential of a cyclopropane and the reduction potential of DCA, respectively, and $e^2/a\varepsilon$ and $E_{0\text{-}0}$ are the energy of Coulomb force and the excited singlet energy of DCA, respectively.[23] These results are also shown in Table 2. Negative ΔG values were obtained in all cases.

$$\Delta G = 96.4[E(D/D^+)_V - E(A^-/A)_V - e^2/a\varepsilon - E_{0\text{-}0}] \quad (\text{kJ/mol}) \qquad (8)$$

$$DCA \xrightarrow{h\nu} {}^1DCA^* \qquad (13)$$

$$^1DCA^* + CP \longrightarrow [DCA^{\overline{\cdot}} \cdots CP^{\dot{+}}] \qquad (14)$$

$$[DCA^{\overline{\cdot}} \cdots CP^{\dot{+}}] \longrightarrow DCA + CP \qquad (15)$$

$$[DCA^{\overline{\cdot}} \cdots CP^{\dot{+}}] \longrightarrow DCA^{\overline{\cdot}} + CP^{\dot{+}} \qquad (16)$$

$$DCA^{\overline{\cdot}} + CP^{\dot{+}} \longrightarrow DCA + CP \qquad (17)$$

$$^1DCA^* + ArH \longrightarrow [DCA^{\overline{\cdot}} \cdots ArH^{\dot{+}}] \qquad (18)$$

$$[DCA^{\overline{\cdot}} \cdots ArH^{\dot{+}}] \longrightarrow DCA + ArH \qquad (19)$$

$$[DCA^{\overline{\cdot}} \cdots CP^{\dot{+}}] + ArH \rightarrow DCA^{\overline{\cdot}} + [CP \cdots ArH]^{\dot{+}} \qquad (20)$$

$$[DCA^{\overline{\cdot}} \cdots ArH^{\dot{+}}] + CP \rightarrow DCA^{\overline{\cdot}} + [CP \cdots ArH]^{\dot{+}} \qquad (21)$$

$$[CP \cdots ArH]^{\dot{+}} \longrightarrow CP^{\dot{+}} + ArH \qquad (22)$$

Scheme 5.

DISCUSSION

Primary process

We have shown, in the preceding section, that the fluorescence of DCA is quenched by the cyclopropane derivatives (CP) almost at a diffusion controlled rate and the one-electron transfer from CP to $^1\mathrm{DCA}^*$ in acetonitrile is estimated to be exothermic. These results strongly suggest that, in the DCA-sensitized photoreactions of CP, the ion radical pair $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{CP}^{+\cdot}]$ is produced spontaneously upon excitation of DCA, specifically in polar solvent. The solvent effects on the photo-oxygenation of CP also support the involvement of electron transfer and the participation of an ion radical pair in the photoreaction in polar solvent.

However, in general, the separation of a radical ion pair $[\mathrm{A}^{-\cdot}\ldots\mathrm{D}^{+\cdot}]$ into dissociated ion radicals $\mathrm{A}^{-\cdot}$ and $\mathrm{D}^{+\cdot}$ is a critical factor determining the efficiency of the photo-induced electron transfer reaction, since a major quenching process of the ion radical pair is the back-electron transfer from $\mathrm{A}^{-\cdot}$ to $\mathrm{D}^{+\cdot}$. Recently, we have proposed that the separation may be facilitated by the addition of some additives through the mode of Eqs 9–12, where X and Y are the additives that stabilize $\mathrm{A}^{-\cdot}$ and $\mathrm{D}^{+\cdot}$ by interaction with the respective ion radical species. In fact, we found that the DCA-sensitized photoisomerization of **1c** was remarkably accelerated by the addition of molecular dioxygen and/or aromatic hydrocarbons, which may act as X and Y, respectively.[16]

$$\mathrm{A}+\mathrm{D}\xrightarrow{h\nu}[\mathrm{A}^{-\cdot}\ldots\mathrm{D}^{+\cdot}] \qquad (9)$$

$$[\mathrm{A}^{-\cdot}\ldots\mathrm{D}^{+\cdot}]+\mathrm{X}\rightarrow[\mathrm{A}\ldots\mathrm{X}]^{-\cdot}+\mathrm{D}^{+\cdot} \qquad (10)$$

$$[\mathrm{A}^{-\cdot}\ldots\mathrm{D}^{+\cdot}]+\mathrm{Y}\rightarrow\mathrm{A}^{-\cdot}+[\mathrm{D}\ldots\mathrm{Y}]^{+\cdot} \qquad (11)$$

$$[\mathrm{A}^{-\cdot}\ldots\mathrm{D}^{+\cdot}]+\mathrm{X}+\mathrm{Y}\rightarrow[\mathrm{A}\ldots\mathrm{X}]^{-\cdot}+[\mathrm{D}\ldots\mathrm{Y}]^{+\cdot} \qquad (12)$$

During this research, we have found that the photo-oxygenation of CP is also accelerated by the addition of aromatic hydrocarbons. The results can be explained in terms of the mechanism shown in Scheme 5.

The fluorescence of DCA in acetonitrile is quenched by aromatic hydrocarbons (ArH) at almost a diffusion controlled rate. The free energy changes (ΔG) for the electron transfer process from ArH to $^1\mathrm{DCA}^*$ are also negative (Table 2). Consequently, two competitive electron transfer processes, both of which are exothermic, are likely to be involved in the DCA-sensitized photoreaction of CP in the presence of ArH, giving the corresponding two ion radical pairs, $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{CP}^{+\cdot}]$ and $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{ArH}^{+\cdot}]$. The hole transfer from $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{ArH}^{+\cdot}]$ to CP is apparently exothermic, since the oxidation potentials of CP are lower than those of ArH. Moreover, interaction between $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{CP}^{+\cdot}]$ and ArH may possibly force the separation of $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{CP}^{+\cdot}]$ into $\mathrm{CP}^{+\cdot}$ probably through the π-complexation between $\mathrm{CP}^{+\cdot}$ and ArH in a manner similar to that reported by Majima *et al.*,[19] although this process is endothermic.

On the other hand, the fluorescence of DCA was not quenched by $\mathrm{LiBF_4}$ or $\mathrm{Mg(ClO_4)_2}$ and the rate constant of this fluorescence quenching was not affected by the addition of these metal salts. Therefore, it is considered that the ion radical pair $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{CP}^{+\cdot}]$ generated primarily dissociates into the free ion radicals, $\mathrm{DCA}^{-\cdot}$ and $\mathrm{CP}^{+\cdot}$, with the aid of the metal salts, where the metal cation serves as X and its gegen anion as Y (Eqs 9–12 and 23). The detailed mechanisms of the metal salt effects on the DCA-sensitized electron transfer reactions will be discussed in a separate paper.[24]

$$\begin{array}{l}
[\mathrm{DCA}^{\cdot -}\cdots\mathrm{CP}^{\cdot +}] + \mathrm{M}^+\mathrm{Z}^- \longrightarrow [\mathrm{DCA}^{\cdot -}\cdots\mathrm{M}^+] + [\mathrm{CP}^{\cdot +}\cdots\mathrm{Z}^-] \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\downarrow \qquad\qquad\qquad (23) \\
\mathrm{M}^+\mathrm{Z}^-\ ;\ \text{Metal Salt} \qquad\qquad\qquad \mathrm{DCA}^{\cdot -} + \mathrm{CP}^{\cdot +} + \mathrm{M}^+\mathrm{Z}^-
\end{array}$$

The fluorescence of DCA was also quenched by TEA and DABCO in diffusion controlled rates and the free energy changes for the one-electron transfer from the amines to $^1\mathrm{DCA}^*$ were negative. The formation of 1,2-dioxolanes was completely quenched by the addition of the amines. The oxidation potentials of TEA and DABCO were lower than those of CP. These results suggest that, in the DCA-sensitized photo-oxygenation of CP in the presence of amines, two ion radical pairs, $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{CP}^{+\cdot}]$ and $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{amine}^{+\cdot}]$, are produced competitively. However, it is expected that $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{CP}^{+\cdot}]$ and also the free ion radical $\mathrm{CP}^{+\cdot}$ are efficiently quenched by the amines in an exothermic manner. As a result, the whole transfer from $[\mathrm{DCA}^{-\cdot}\ldots\mathrm{amine}^{+\cdot}]$ and $\mathrm{amine}^{+\cdot}$ to CP does not occur, hence, the photoreaction is quenched.

Oxygenation pathways

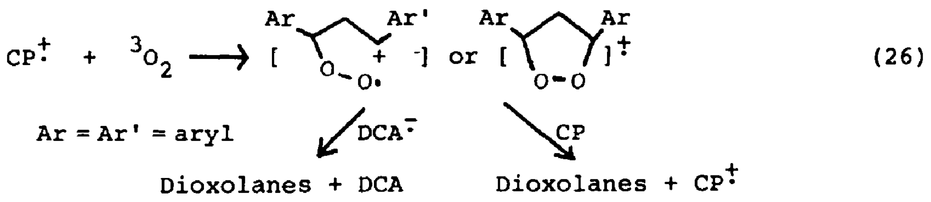
The above discussion strongly indicates that the DCA-sensitized photo-oxygenation of CP is initiated by the one-electron transfer from CP to $^1\mathrm{DCA}^*$ to give $\mathrm{CP}^{+\cdot}$ as reactive species. The plausible mechanisms of the oxygenation processes based on this assumption are now presented in Scheme 6.

The first mechanism (Eqs 24 and 25) involves the reaction between $\mathrm{CP}^{+\cdot}$ and $\mathrm{O}_2^{-\cdot}$ that can be generated by electron transfer from $\mathrm{DCA}^{-\cdot}$ to $^3\mathrm{O}_2$, as has been suggested by Foote *et al.*[1]

The second mechanism (Eq. 26) involves the whole transfer from CP to the intermediate which is generated by the reaction between $\mathrm{CP}^{+\cdot}$ with $^3\mathrm{O}_2$.[2,11] However, such a whole transfer does not occur with less electron-rich CP such as **1h**–**1j**. In support of this mechanism, the quantum yields for the formation of **3c** and **4c** exceeded one (Table 5). In this case, the quantum efficiency in the presence of Phen and $\mathrm{Mg(ClO_4)_2}$ was much higher than that in the absence of these additives. The enhancement of this quantum efficiency could be explained by the effective formation of solvent separated $\mathrm{CP}^{+\cdot}$ and also by the suppression of back-electron transfer from $\mathrm{DCA}^{-\cdot}$ to $\mathrm{CP}^{+\cdot}$. The chain transfer mechanism was also supported by the fact that the reaction of **1c** with $^3\mathrm{O}_2$ in the presence of a catalytic amount of

$$\mathrm{DCA}^{\overset{-}{\cdot}} + {}^3\mathrm{O}_2 \longrightarrow \mathrm{DCA} + \mathrm{O}_2^{\overset{-}{\cdot}} \quad (24)$$

$$\mathrm{CP}^{\overset{+}{\cdot}} + \mathrm{O}_2^{\overset{-}{\cdot}} \longrightarrow \text{Dioxolanes} \quad (25)$$



Scheme 6.

$Ph_3C^+BF^-$ in acetonitrile in the dark affords **3c** and **4c** in 60–70% yields. In this reaction, the cation radical generated by the electron transfer from **1c** to Ph_3C^+ is involved as a key intermediate and it is converted into **3c** and **4c** by reaction with $^3O_2$ via the pathways of Eq. (26).

Comparison with the oxidation by singlet oxygen†

It seems important to examine the possibility of the participation of singlet oxygen as a reactive species in the DCA-sensitized photo-oxygenation of CP, since singlet oxygen can be generated by energy transfer from $^3DCA^*$ to $^3O_2$ or by the back-electron transfer from $O_2^{\cdot-}$ to $CP^{+\cdot}$. With this in mind, the photo-oxygenation of **1c** and **1j** was carried out using methylene blue (MB) and Rose Bengal (RB) as sensitizers. Irradiation of an acetonitrile solution of **1c** in the presence of MB or RB with a tungsten lamp (>500 nm) under an oxygen stream slowly gave **3c** and **4c** in 50–60% yields. The same products were also obtained by RB-sensitized photo-oxidation in dichloromethane and ethyl acetate in low yields (<30%). In contrast, these products were not obtained by DCA-sensitized photo-oxygenation in these solvents. Similar irradiation of **1j** in the presence of MB or RB gave no oxidized products at all, with a quantitative recovery of the starting material even after prolonged irradiation.

The reactivity of other singlet oxygen sources was also examined. Treatment of **1c** with the endoperoxide of 1,4-dimethylnaphthalene[26] in dichloromethane or with a triphenylphosphite ozone adduct[27] in dichloromethane afforded a small amount of 4-methoxybenzaldehyde (**6c**, <10%).

Table 5. Quantum yields for the formation of **3c** and **4c** in the absence or presence of additives[a]

Additive	Concentration of additive (mol/l)	Quantum yield (ϕ)
None		1.6
Phen	0.025	3.7
$LiBF_4$	0.025	2.8
$Mg(ClO_4)_2$	0.025	5.8
TEA	0.005	0
DABCO	0.005	0

[a] [**1c**] = 0.025 mol/l in acetonitrile under an O_2 atmosphere.

From these results, it is concluded that singlet oxygen is not involved as a principal reactive species in the DCA-sensitized photo-oxygenation of **1c** and **1j**.

Finally, it may be pointed out that the DCA-sensitized photo-oxygenation of CP provides an excellent methodology for the preparation of 3,5-diaryl-1,2-dioxolanes which are not otherwise easily accessible.[28] In this methodology the following conclusions can be made. (1) Chemical yields as well as quantum efficiency for the formation of the dioxolanes are high, especially for CP bearing electron-donating substituents. In addition, this photo-oxidation enables a gram-scale preparation of 1,2-dioxolane derivatives. (2) The reaction can be accomplished under very mild conditions. (3) The dioxolanes can be easily isolated by recrystallization of the crude reaction mixture.

EXPERIMENTAL

General. M.ps were taken on a hot stage and are uncorrected. ^{1}H-NMR spectra were recorded on Hitachi Perkin–Elmer R-24 (60 MHz) and JEOL JS-100 NMR spectrometers for solns in CCl_4 or $CDCl_3$ containing TMS as internal standard. IR spectra were obtained on a Hitachi IRA-16 spectrometer, mass spectra on a Hitachi RMU-6E spectrometer, UV spectra on a Hitachi 124 spectrophotometer and fluorescence spectra on a JASCO FP-500 spectrofluorometer.

Analytical GLC was performed with a Hitachi 164 instrument. GLC analyses were carried out using 1 m × 3 mm columns packed with 10% SE 30 and 10% PEG 4000 on Shimarite W.

Oxidation and reduction potentials were measured in argon–saturated acetonitrile solns at $20 \pm 0.1°$ by cyclic voltammetry using a NICHIA NP-G 2550 potentiostat and Ag/Ag^+ reference electrode. Tetraethylammonium perchlorate (0.1 mol/l) was used as a supporting electrolyte.

Quantum yields were determined by the procedure of Murov[29] using a potassium ferrioxalate actinometer. The light source was a 500 W high-pressure Hg lamp and the 405 nm Hg line was isolated through an aq NH_3–$CuSO_4$ filter soln. The light intensity was determined twice before and once after actual photoreactions. No change in light intensity was observed during experiments. For the quantum yield determination, photoreactions were carried out up to <10% conversion of the starting materials and the reaction mixtures analysed by GLC. The quantum yields were determined three times and averaged. The photo-oxygenation of **1c** in the absence of an additive was used as a reference for quantum

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† The MB-sensitized photo-oxygenation of the cyclopropanes may involve the electron transfer process from the substrates to the excited MB.[25]

yield determination of photo-oxygenation in the presence of additives.

Materials. Acetonitrile, propionitrile and butyronitrile were distilled three times over P_2O_5 and then once over anhyd K_2CO_3 before use. Spectro-grade benzene and EtOAc were distilled before use. 1,2-Diarylcyclopropanes were prepared by methods described in the lit.[30,31] and their physical properties are shown below. Other organic chemicals were purchased and purified by distillation or recrystallization. Inorganic chemicals were also purchased and used without further purification.

Physical properties of 1,2-diarylcyclopropanes. trans-**1a**: m.p. 132.0–133.5°; *m/z* 267 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.28 (2H, dd, J = 6 and 9 Hz), 2.00 (2H, dd), 2.85 (6H, s), 3.70 (3H, s), 6.76 (4H, ABq, $\Delta\nu$ = 15 Hz, J = 9 Hz), 6.84 (4H, ABq, $\Delta\nu$ = 24 Hz, J = 9 Hz).

trans-**1b**: m.p. 39.0–41.0°; *m/z* 237 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.28 (2H, dd, J = 6 and 9 Hz), 2.00 (2H, dd), 2.88 (6H, s), 6.80 (4H, ABq, $\Delta\nu$ = 24 Hz, JAB = 9 Hz), 7.2 (4H, s).

trans-**1c**: m.p. 69.5–70.5°; *m/z* 254 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.25 (2H, dd, J = 6 and 9 Hz), 1.98 (2H, dd), 3.70 (6H, s), 6.82 (8H, ABq, $\Delta\nu$ = 16 Hz, J = 9 Hz).

trans-**1d**: m.p. 98.0–99.0°; *m/z* 314 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.20 (2H, dd, J = 6 and 9 Hz), 1.90 (2H, dd), 3.70 (12H, s), 6.50 (6H, s).

trans-**1e**: m.p. 30.5–32.0°; *m/z* 238 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.30 (2H, dd, J = 6 and 9 Hz), 2.03 (2H, dd), 2.26 (3H, s), 3.70 (3H, s), 6.89 (4H, ABq, $\Delta\nu$ = 17 Hz, J = 9 Hz), 6.98 (4H, s).

trans-**1f**: m.p. 53.0–54.0°; *m/z* 258 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.32 (2H, dd, J = 6 and 9 Hz), 2.02 (2H, dd), 3.72 (3H, s), 6.90 (4H, ABq, $\Delta\nu$ = 15 Hz, J = 9 Hz), 7.08 (4H, ABq, $\Delta\nu$ = 12 Hz, J = 9 Hz).

trans-**1g**: m.p. 80.0–81.0° (lit. 82.5–83.5°);[31] *m/z* 224 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.24 (2H, dd, J = 6 and 9 Hz), 1.98 (2H, dd), 3.65 (3H, s), 6.73 (4H, ABq, $\Delta\nu$ = 21 Hz, J = 9 Hz), 6.98 (5H, s).

trans-**1h**: m.p. 55.5–56.0°; *m/z* 222 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.29 (2H, dd, J = 6 and 9 Hz), 1.98 (2H, dd), 2.25 (6H, s), 6.85 (8H, s).

trans-**1i**: m.p. 81.5–82.0°; *m/z* 262 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.30 (2H, dd, J = 6 and 9 Hz), 1.98 (2H, dd), 6.95 (8H, ABq, $\Delta\nu$ = 13 Hz, J = 9 Hz).

trans-**1j**:[30] b.p. 149–151/7 mmHg; *m/z* 194 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.36 (2H, dd, J = 6 and 9 Hz), 2.08 (2H, dd), 7.03 (10H, s).

cis-**2c**: m.p. 55.5–56.0°; *m/z* 254 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ 1.25 (2H, dd, J = 6 and 9 Hz), 2.30 (2H, dd), 3.60 (6H, s), 6.57 (8H, ABq, $\Delta\nu$ = 14 Hz, J = 9 Hz).

General procedure for DCA-sensitized photo-oxygenation of 1,2-diarylcyclopropanes. A soln of a cyclopropane derivative (0.025 mol/l) and DCA (1×10^{-4} mol/l) in an appropriate solvent in the absence or presence of an additive at ambient temp (*ca* 35°) was irradiated with a 500 W high pressure Hg arc through an aq NH_3–$CuSO_4$ filter soln[29] under an O_2 atmosphere. The progress of the photoreaction was followed by GLC. After consumption of the cyclopropane, the solvent was removed and the residue analysed on the basis of its ^{1}H-NMR spectral data, from which the product ratio was determined by integration of the signals. The dioxolanes were obtained by repeated recrystallizations of the residue from hexane. The yields are listed in Tables 1 and 3.

Typical procedure for DCA-sensitized photo-oxygenation of 1,2-diarylcyclopropanes. A soln of **1c** (127 mg, 0.5 mmol) and DCA (0.57 mg, 0.0025 mmol) in anhyd acetonitrile (10 ml) was irradiated for 1 hr with O_2 bubbling through and the solvent then removed. ^{1}H-NMR analysis of the residue revealed the formation of **3c** and **4c** (**3c**–**4c** = 0.3) in 95% yield. Warm hexane (< 50°) was then added to the residue. Sparingly soluble DCA was filtered off and the filtrate cooled to give a mixture of **3c** and **4c**, which was then recrystallized from hexane to give the pure compounds (130 mg, 84%).

Photoreaction of **3c** *and* **4c**. A soln of a mixture of **3c** and **4c** (57 mg, 0.2 mmol) and DCA (2.3 mg, 0.01 mmol) in acetonitrile (8 ml) was irradiated for 3 hr under a N_2 atmosphere through an aq NH_3–$CuSO_4$ filter soln. The progress of the photoreaction was followed by TLC. After evaporation of the solvent, ^{1}H-NMR analysis of the residue revealed the formation of **5c**, **6c** and **7c** in a 4:2:1 ratio. The residue was chromatographed on silica gel. Elution with EtOAc–benzene (2:8) gave 20 mg (40%) of **5c**. **5c**: solid; *m/z* 286 ($[M]^+$, vw), 150, 136; IR ν_{max}^{neat} C=O 1660 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.23 (2H, d, J = 6 Hz), 3.72 (3H, s), 3.77 (3H, s), 5.18 (1H, t, J = 6 Hz), 7.00 (4H, ABq, $\Delta\nu$ = 26 Hz, J = 8 Hz), 7.29 (4H, ABq, $\Delta\nu$ = 60 Hz, J = 8 Hz).

Thermolysis of **3c** *and* **4c**. A soln of a mixture of **3c** and **4c** (50 mg) in benzene was refluxed for 2 hr under a N_2 atmosphere. After evaporation of benzene, ^{1}H-NMR analysis of the mixture revealed the formation **6c** and **7c** (55%) in a 1:1 ratio.

Reduction of **3c** *and* **4c** *by* $NaBH_4$. A soln of a mixture of **3c** and **4c** (228 mg, 0.8 mmol) and $NaBH_4$ (68 mg, 1.8 mmol) in EtOH (20 ml) was stirred for 24 hr at room temp. The mixture was extracted with 100 ml of diethyl ether. The ether extract was washed with NaCl aq, dried and filtered. After evaporation of the ether, ^{1}H-NMR analysis of the mixture revealed the formation of 1,3-bis(4-methoxyphenyl)propan-1,3-diol as a mixture of the *meso* and *dl* isomers (**8c** and **9c**), **10c** and **11c** in 1:1:1 ratio. The mixture was chromatographed on silica gel. Elution with EtOAc–benzene gave **10c** and **11c** (106 mg, 46%). Elution with EtOAc–benzene (2:8) gave **8c** and **9c** (89 mg, 38%). Recrystallization from benzene–hexane gave the analytical sample of **9c**: m.p. 64.5–66°; *m/z* 288 $[M]^+$; IR ν_{max}^{OH} 3310 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.85–2.25 (2H, m), 2.83 (2H, s), 3.74 (6H, s), 4.7–5.0 (2H, m), 7.00 (8H, ABq, $\Delta\nu$ = 24 Hz, J = 9 Hz).

Pyrene-sensitized photo-oxygenation of **1c** *in the presence of* p-*DCB*. A soln of **1c** (51 mg, 0.2 mmol), pyrene (20 mg, 0.1 mmol) and *p*-DCB (13 mg, 0.1 mmol) in acetonitrile (8 ml) was irradiated under an O_2 atmosphere. The progress of the photoreaction was followed by GLC. After evaporation of the solvent, the residue was analysed on the basis of its ^{1}H-NMR spectral data.

Physical properties of 1,2-dioxolanes. cis-**4a**: solid (< 40°); *m/z* 299 ($[M]^+$, vw), 163, 150, 149, 136; ^{1}H-NMR ($CDCl_3$) δ 2.2–3.5 (2H, m), 2.80 (6H, s), 3.68 (3H, s), 5.10 (1H, t, J = 7.5 Hz), 5.20 (1H, t), 6.3–7.5 (8H, m).

cis-**4b**: oil; *m/z* 269 ($[M]^+$, vw), 163, 149, 120, 106; ^{1}H-NMR ($CDCl_3$) δ 2.5–3.6 (2H, m), 2.85 (6H, s), 5.40 (2H, t, J = 7.5 Hz), 6.5–7.5 (9H, m).

trans-**3c**: m.p. 122–124° (dec); *m/z* 286 ($[M]^+$, vw), 150, 136; IR ν_{max}^{KBr} 2860, 1250 and 1130 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.92 (2H, t, J = 7.5 Hz), 3.79 (6H, s), 5.40 (2H, t), 7.05 (8H, ABq, $\Delta\nu$ = 25 Hz, J = 9 Hz); ^{13}C-NMR ($CDCl_3$) δ 50.3, 55.3, 83.1, 114.1, 128.4, 129.9, 159.9. (Found: C, 71.00; H, 6.29%. Calc for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.)

cis-**4c**: m.p. 92–94° (dec); *m/z* 286 ($[M]^+$, vw), 150, 136; ^{1}H-NMR ($CDCl_3$) δ 2.65 (1H, dt, J = 12.3 and 7.5 Hz), 3.34 (1H, dt), 3.76 (6H, s), 5.37 (2H, t), 7.05 (8H, ABq, $\Delta\nu$ = 25 Hz, J = 9 Hz); ^{13}C-NMR ($CDCl_3$) δ 51.2, 55.3, 83.2, 114.1, 128.1, 130.5, 159.5. (Found: C, 71.16; H, 6.35. Calc for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.)

cis-**4d**: oil; *m/z* 346 ($[M]^+$, vw), 180, 166; ^{1}H-NMR ($CDCl_3$) δ 2.5–3.6 (2H, m), 3.75 (12H, s), 5.30 (2H, t, J = 7.5 Hz), 6.2–7.0 (6H, m).

cis-**4e**: m.p. 89–91° (dec); *m/z* 270 ($[M]^+$, vw), 150, 136, 134, 120; ^{1}H-NMR ($CDCl_3$) δ 2.24 (3H, s), 2.5–3.3 (2H, m), 3.60 (3H, s), 5.27 (2H, t, J = 7.5 Hz), 6.7–7.5 (8H, m). (Found: C, 75.24; H, 6.86%. Calc for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.)

cis-**4f**: m.p. 97–99° (dec); *m/z* 280 ($[M]^+$, vw), 150, 144, 136, 130; ^{1}H-NMR ($CDCl_3$) δ 2.4–3.7 (2H, m), 3.75 (3H, s), 5.35 (2H, t, J = 7.5 Hz), 6.7–7.5 (8H, m). (Found: C, 66.38; H, 5.00. Calc for $C_{16}H_{15}O_3Cl$: C, 66.09; H, 5.19%.)

trans-**3g**: m.p. 84–86° (dec); *m/z* 256 ($[M]^+$, vw), 150, 136, 120, 106; ^{1}H-NMR ($CDCl_3$) δ 2.97 (2H, t, J = 7.5 Hz), 3.78 (3H, s), 5.3–5.5 (2H, m), 7.06 (4H, ABq, $\Delta\nu$ = 25 Hz, J = 9 Hz), 7.3–7.5 (5H, m).

cis-**4g**: m.p. 48–49.5° (dec); *m/z* 256 ($[M]^+$, vw), 150, 136, 120, 106; ^{1}H-NMR ($CDCl_3$) δ 2.65 (1H, dt, J = 12.5 and 7.5

Hz), 3.39 (1H, dt), 3.76 (3H, s), 5.3–5.5 (2H, m), 7.06 (4H, ABq, $\Delta\nu = 25$ Hz, $J = 9$ Hz), 7.3–7.5 (5H, m). (Found: C, 74.69; H, 6.26. Calc for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.)

Oxygenation of **1c** *in the presence of* $Ph_3C^+BF_4^-$.[32] A soln of $Ph_3C^+BF_4^-$ (36 mg, 0.11 mmol) and **1c** (254 mg, 1.0 mmol) in anhyd acetonitrile (50 ml) under an O_2 atmosphere was stirred for 24 hr at room temp. After evaporation of the solvent, ^{1}H-NMR and GLC analyses of the residue showed the formation of **3c** and **4c** in a 1:1 ratio, which was recrystallized from hexane to give the pure compounds (210 mg, 73%).

Dye-sensitized photo-oxygenation of **1c** *and* **1j**. A soln of **1c** or **1j** (50 mg, 0.2 mmol) containing RB or MB (2 mg) in an appropriate solvent (8 ml) was irradiated with a tungsten lamp under an O_2 atmosphere. The progress of the photoreaction was followed by GLC. After evaporation of the solvent, the residue was analysed on the basis of its ^{1}H-NMR spectral data.

Oxygenation with triphenylphosphite ozone adduct.[27] A soln of triphenylphosphite (310 mg, 1 mmol) in dichloromethane (50 ml) was ozonized at −70°. After purging with N_2, a soln of **1c** (127 mg, 0.5 mmol) in dichloromethane (25 ml) was added and the mixture warmed to room temp. After evaporation of the solvent, ^{1}H-NMR analysis of the residue showed it to contain triphenylphosphate as a major product along with a small amount of 4-methoxybenzaldehyde (**6c**, <3%) and unchanged **1c** (>95%).

Oxygenation with the endoperoxide of 1,4-dimethylnaphthalene.[26] A soln of the endoperoxide of 1,4-dimethylnaphthalene (40 mg, 0.2 mmol) and **1c** (50 mg, 0.2 mmol) in dichloromethane (30 ml) was refluxed for 5 hr under a N_2 atmosphere. After evaporation of the solvent, ^{1}H-NMR and GLC analyses of the residue showed that **1c** was quantitatively recovered together with 1,4-dimethylnaphthalene.

Gram-scale preparation of the 1,2-dioxolanes.

(a) A soln of **1c** (2.54 g, 10 mmol), 1-methylnaphthalene (0.71 g, 5 mmol) and DCA (4.6 mg, 0.02 mmol) in anhyd acetonitrile (100 ml) was irradiated for 1 hr with O_2 bubbling through. After removal of the solvent, the residue was recrystallized from hexane to give a mixture of **3c** and **4c** (2.43 g) in 85% yield.

(b) A soln of **1f** (1.29 g, 5 mmol), $LiBF_4$ (235 mg, 2.5 mmol) and DCA (2.3 mg, 0.01 mmol) in 50 ml of anhyd acetonitrile was irradiated for 1 hr with O_2 bubbling through. After removal of the solvent, the residue was recrystallized from hexane to give a mixture of **3f** and **4f** (1.30 g, 90%).

Acknowledgements—We are grateful to the Asahi Glass Foundation and for a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan for partial financial support of this research.

REFERENCES

[1] J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.* **102**, 6083 (1980); J. Steichen and C. S. Foote, *Ibid.* **103**, 1855 (1981).

[2a] D. H. R. Barton, R. K. Haynes, G. Leclerc, P. D. Magnus and I. D. Menzies, *J. Chem. Soc. Perkin Trans 1* 2055 (1975); [b] R. Tang, H. J. Tue, J. P. Wolfe and F. Mares, *J. Am. Chem. Soc.* **100**, 5248 (1978).

[3] I. Saito, T. Matsuura and K. Inoue, *J. Am. Chem. Soc.* **103**, 188 (1981) and **105**, 3200 (1983).

[4] S. L. Mattes and S. Farid, *Ibid.* **104**, 1454 (1982).

[5a] S. L. Mattes and S. Farid, *J. Chem. Soc. Chem. Commun.* 457 (1980); [b] N. Berenjian, P. deMayo, F. H. Phoenix and A. C. Weedon, *Tetrahedron Lett.* 4179 (1979).

[6] W. Ando, T. Nagashima, K. Saito and S. Kohmoto, *J. Chem. Soc. Chem. Commun.* 154 (1979).

[7] I. Saito, K. Tamoto and T. Matsuura, *Tetrahedron Lett.* 2889 (1979).

[8] O. Yonemitsu, *Yakugaku Zassi* **102**, 716 (1982).

[9] K. Mizuno, K. Murakami, N. Kamiyama and Y. Otsuji, *J. Chem. Soc. Chem. Commun.* 462 (1983).

[10a] A. P. Schaap, B. K. Zaklika and L. W.-M. Fung, *J. Am. Chem. Soc.* **102**, 389 (1980); [b] A. P. Schaap, L. Lopez and S. D. Gagnon, *Ibid.* **105**, 663 (1983); [c] A. P. Schaap, S. Siddiqui, S. D. Gagnon and L. Lopez, *Ibid.* **105**, 5149 (1983); [d] A. P. Schaap, L. Lopez, S. D. Anderson and S. D. Gagnon, *Tetrahedron Lett.* **23**, 5493 (1982); [e] A. P. Schaap, C. Prasad and S. D. Gagnon, *Ibid.* **24**, 3047 (1983).

[11] S. Futamura, S. Kusunose, H. Ohta and Y. Kamiya, *J. Chem. Soc. Chem. Commun.* 1223 (1982); *J. Chem. Soc. Perkin Trans. 1* 15 (1984).

[12] G. P. Kirschenheuter and G. W. Griffin, *J. Chem. Soc. Chem. Commun.* 596 (1983).

[13] Y. Takahashi, T. Miyashi and T. Mukai, *J. Am. Chem. Soc.* **105**, 6511 (1983).

[14a] S. Ito, H. Takeshita, M. Hiyama and Y. Fukazawa, *Tetrahedron Lett.* 9 (1972); [b] T. Kobayashi, M. Kodama and S. Ito, *Ibid.* 655 (1975); [c] R. H. Rynbrandt and F. E. Dutton, *J. Org. Chem.* **40**, 3079 (1975).

[15] K. Mizuno, N. Kamiyama and Y. Otsuji, *Chem. Lett.* 477 (1983).

[16] K. Mizuno, J. Hiromoto, K. Ohnishi and Y. Otsuji, *Chem. Lett.* 1059 (1983).

[17a] P. C. Wong and D. R. Arnold, *Tetrahedron Lett.* 2181 (1979); [b] H. D. Roth and M. L. M. Schilling, *J. Am. Chem. Soc.* **102**, 7956 (1980) and **103**, 7120 (1981).

[18a] K. A. Brown-Wensley, S. L. Mattes and S. Farid, *Ibid.* **100**, 4162 (1978); [b] D. S. Steichen and C. S. Foote, *Ibid.* **103**, 1855 (1981); [c] S. L. Mattes and S. Farid, *Acc. Chem. Res.* **15**, 80 (1982).

[19a] T. Majima, C. Pac and H. Sakurai, *J. Am. Chem. Soc.* **102**, 5265 (1980) and **103**, 4499 (1981); [b] C. Pac, J. Kubo, T. Majima and H. Sakurai, *Photochem. Photobiol.* **36**, 273 (1982).

[20] T. Asanuma, T. Gotoh, A. Tsuchida, M. Yamamoto and Y. Nishijima, *J. Chem. Soc. Chem. Commun.* 485 (1977).

[21] S. Tazuke and N. Kitamura, *Ibid.* 515 (1977).

[22] J. Eriksen and C. S. Foote, *J. Phys. Chem.* **82**, 2659 (1978).

[23] D. Rehm and A. Weller, *Isr. J. Chem.* **8**, 259 (1970).

[24] K. Mizuno, N. Ichinose and Y. Otsuji, *Chem. Lett.* (1985), submitted for publication.

[25] L. Manring, J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.* **102**, 4275 (1980).

[26] H. H. Wasserman and D. L. Larsen, *J. Chem. Soc. Chem. Commun.* 253 (1972).

[27] R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.* **91**, 5358 (1969).

[28a] W. Adam, A. Birke, C. Cadiz, S. Diaz and A. Rodriguez, *J. Org. Chem.* **43**, 1154 (1978); [b] M. Yoshida, M. Miura, M. Nojima and S. Kusabayashi, *J. Am. Chem. Soc.* **105**, 6279 (1983).

[29] S. L. Murov, *Handbook of Photochemistry*, pp. 95 and 119. Marcel Dekker, New York (1973).

[30] S. G. Beach, J. H. Turnbull and W. Wilson, *J. Chem. Soc.* 4686 (1952).

[31] S. S. Hixson and D. W. Garrett, *J. Am. Chem. Soc.* **96**, 4872 (1974).

[32] H. J. Dauben, J. Lewis, R. Honnen and K. M. Harmon, *J. Org. Chem.* **25**, 1442 (1960).